

20-2-24/60

Anionotropic Rearrangement of Substituted Perfluoropropenes

tions of perfluorallylchloride $\text{CF}_2=\text{CF}-\text{CF}_2\text{Cl}$. There also exists information according to which influence of nucleophile reagents on perfluorallylchloride leads to a substitution of chlorine by a corresponding anion. It has to be assumed that this is the result of the conjugation of the bond C-Cl with the double bond. The authors of the present paper investigated the reactions of perfluorallylchloride with sodium methylate and diethylamine. The interaction with the sodium methylate leads to the perfluorallylmethylether. This reaction represents a new solution for arriving at the derivatives of the perfluoracrylic acid. The ether is polymerized even at a lower temperature. The reaction of perfluorallylchloride with diethylamine has a light course. The perfluorallyldiethylamine produced as result of this reaction rearranges itself, still during the reaction, into perfluorpropenyldiethylamine. Hydrolysis of the latter leads to diethylamide of the α -hydroperfluorpropionic acid. Bromination of the perfluorpropenyldiethylamine with a subsequent hydrolysis results in diethylamide of the α -bromoperfluorpropionic acid. The above isomerization represents an allylic rearrangement and probably is caused by the tendency towards formation of a stabler system, and this owing to the conjugation of a double bond

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with an unseparated electron pair of the substituent in the allylic position. The velocity of the rearrangement depends of the degree of mobility of the electron pair. Different compounds are arranged in a series in accordance with the criterion of stability. The experimental part of the paper under review contains the production methods together with the constants and yields of the substances investigated. There are 3 references, 1 of which is Soviet..

SUBMITTED: January 18, 1957

AVAILABLE: Library of Congress

Card 3/3

DYATKIN, B. L.: Master Chem Sci (diss) -- "The conjugation of bonds in poly-fluoro olefins". Moscow, 1958. 12 pp (Acad Sci USSR, Inst of Organoelemental Compounds), 150 copies (KL, No 6, 1959, 126)

62-58-3-6/30

AUTHORS: Knunyants, I. L. , Sterlin, R. N. , Pinkina, L. N. ,
Dyatkin, B. L.

TITLE: Reactions of Fluorolefins (Reaktsii ftorolefinov)
Communication 7. Addition Compounds of Acid Chlorides to
Vinylidene Fluoride and Trifluoroethylene (Soobshcheniye 7.
Prisoyedineniye khlorangidriđov kislot k ftoristomu vinili-
denu i triftoretilenu)

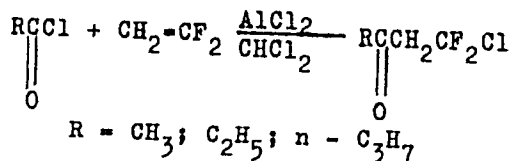
PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk,
1958, Nr 3, pp. 296 - 299 (USSR)

ABSTRACT: The addition of alkyl halides discovered by Kondakov was later
developed by others. In the present paper the authors show
that such fluorolefins as vinylidene fluoride and trifluor-
ethylene (in the presence of nonaqueous $AlCl_3$) possess the
capability of combining with carboxyl chlorides and thereby
forming the corresponding fluoro-substituted ketones. Vinyli-
dene fluoride very readily combines with the acid chlorides
of butyric acid and propionic acid at a temperature of
-5 to -10°C in the presence of equivalent quanta of $AlCl$ in

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Reactions of Fluorolefins. Communication. 7. Addition Compounds of Acid Chlorides to Vinylidene Fluoride and Trifluoroethylene 62-58-3-6/30

pure chloroform, where alkyl-2-chloro-2,2-difluoroethylketones with yields of 44,48 and 33 % form:



At the same time substances form which correspond to the products of the partial or complete substitution of fluorine in chlorine and the products of further condensation. The authors obtained: methyl-2-chloro-2,2-difluoroethylketone and methyl-2-chloro-1,2,2-trifluoroethylketone. There are 8 references, 2 of which are Soviet.

SUBMITTED: November 3, 1956

Card 2/2

SOV/63-3-6-30/41

AUTHORS: Knunyants, I.L., Dyatkin, B.L., German, L.S.

TITLE: Reactions of Perfluoroacrylonitril (Reaktsii perftorakrilonitrila)

PERIODICAL: Khimicheskaya nauka i promyshlennost', 1958, Vol III, Nr 6, pp 828-829 (USSR)

ABSTRACT: It has been shown that pure perfluoroacrylonitril easily reacts with methanol and ethanol producing β -alkoxy- α -hydroperfluoropropionitrils. It reacts also with piperidine and aniline in an ether solution producing amine fluorohydrate. There is 1 table and 2 non-Soviet references.

ASSOCIATION: Institut elementarnykh soedineniy Akademii nauk SSSR (Institute of Elemental-Organic Compounds of the USSR Academy of Sciences)

SUBMITTED: July 10, 1958

Card 1/1

AUTHORS: Knunyants, I. L., Dyatkin, B. L. 62-58-5-25/27

TITLE: Interaction of Some Fluorine Olefins With Phenols (Vzaimo-deystviye nekotorykh ftorolefinov s fenolami)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk 1958, Nr 5, pp. 648-650 (USSR)

ABSTRACT: The special character of the binary bond of perfluoroisobutylene and perfluoracrylonitrile consists among other of the fact that these compounds are easily subjected to an interaction with nucleophile reagents. Alcohols associate in this way without alkaline catalysts and without heating. In the case of perfluoroisobutylene, a substitution of the fluorine-vinyl atom into the alkoxy-group takes place. It was therefore of interest to investigate the behavior of these fluorolefines with respect to phenols. In the present report the authors describe the carried out non-catalytic compound of phenol and hydroquinone with fluoroisobutylene and perfluorakrylonitrile. Concluding, the description of the obtaining of phenylperfluorallylester by the interaction of perfluorallylchloride with potassium phenolate is given. There are 1 table and 5 references, 2 of which are Soviet.

Card 1/2

Interaction of Some Fluorine Olefins With Phenols

62-58-5-25/27

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR (Institute for ~~Elemental~~-organic Compounds AS USSR)

SUBMITTED: January 4, 1956

1. Ethylenes---Chemical reactions 2. Phenols---Chemical reactions

Card 2/2

5(3)

AUTHORS:

Knunyants, I. L., Academician,
Dyatkin, B. L., German, L. S.

SOV/20-124-5-28/62

TITLE:

Reactions of Hexafluoro Butadiene-1,3 With Alcohols and Amines
(Reaktsii geksafторbutadiyena-1,3 so spirtami i aminami)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 5, pp 1065-1068
(USSR)

ABSTRACT:

The reactivity of the 1,3-dienes of the perfluoro-carbon series has hardly been investigated (Refs 1-3). The reactions with nucleophilic reagents which very characteristic of fluoro olefins, have hitherto not been investigated in the case of perfluoro butadiene. These reactions are of particular interest for an understanding of the nature of the conjugated bonds in perfluorated dienes. Here, as distinguished from diene hydrocarbons, a negative rather than a positive charge is to be transmitted along the chain. By the interaction of perfluoro butadiene with sodium ethylate in ethanol the authors obtained a substance which separated HF and formed 1,4-diethoxyperfluoro butadiene-1,3 when isolation in a pure condition was attempted. The treatment of the latter compound with concentrated sulphuric acid resulted in the formation of the diethyl esters of

Card 1/3

Reactions of Hexafluoro Butadiene-1,3 With Alcohols
and Amines

SOV/20-124-5-28/62

fluoro ethylene-1,2-dicarboxylic acid. This ester was transformed into 3-carbethoxy-pyrazolone-5 by the action of hydrazine hydrate. Thus, perfluorobutadiene reacts with two alcohol molecules in the presence of alcoholate. In this connection the terminal carbon atoms are subjected to the nucleophilic attack. Heating of perfluoro butadiene with alcohol in the presence of triethylamine causes the addition of one alcohol molecule. The infrared spectrum and the nuclear-magnetic

resonance of F^{19} suggest a 1,4 affiliation. Under mild conditions perfluoro butadiene reacts with the secondary and primary aliphatic amines. With diethylamine it forms the unstable 1-diethylamine-perfluorobutadiene-1,3, which is readily hydrolyzed to form the diethylamide of α -hydroperfluoro vinylacetic acid. A similar reaction is that of perfluoro butadiene with piperidine. By the interaction of perfluoro butadiene with ethylamine and the hydrolysis of the reaction products ethylamide of the last mentioned acid and bis-ethylamide of fluoro ethylene-1,2-dicarboxylic acid was produced. In this case the resulting bis-ethylamide of symmetrical

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Reactions of Hexafluoro Butadiene-1,3 With Alcohols
and Amines

SOV/20-124-5-28/62

difluorosuccinic acid loses only a single HF molecule (as in the case of the ester) and forms a corresponding derivative of fluoro ethylene-1,2-dicarboxylic acid. There are 3 references.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute for Elemental-Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: November 21, 1958

Card 3/3

DYATKIN, B. L.

02040
S/062/60/000/02/03/012
B003/B066

5.3600

AUTHORS:

Knunyants, I. L., German, D. S., Dyatkin, B. L.

TITLE:

Reactions of Fluoro-olefins. 11th Report. Interaction of
Compounds of the Perfluoro Isobutylene Series With Amines
and Ammonia

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 2, pp. 221 - 230

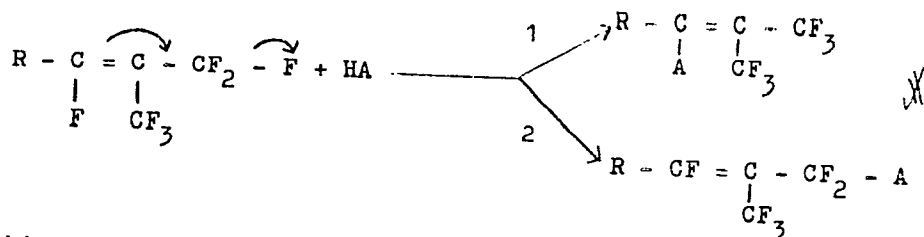
TEXT: The authors investigated the reactions of 1-alkyl-, 1-alkoxy-,
and 1-aryl-perfluoro isobutylenes with amines and ammonia. (The following
compounds were subjected to the experiments: 1-phenyl perfluoro iso-
butylene, 1-phenyl perfluoro propylene, $\alpha, \beta, \beta, \beta$ -tetrafluoro propio-
phenone, 1-phenyl-1,2-dibromo-perfluoro propane, 1-butyl perfluoro iso-
butylene, 1-styryl-perfluoro isobutylene, 1-ethylperfluoroisobutylene, γ -
1-isoamylperfluoroisobutylene, anhydrous ammonia, ammonium hydroxide,
ethyl amine, diethyl amine, and piperidine. The preparation of the com-
pounds and their reactions are described in detail in the experimental
part of the paper.) 1-alkyl- and 1-aryl perfluoro isobutylenes react with

Card 1/3

Reactions of Fluoro-olefins. 11th Report.
Interaction of Compounds of the Perfluoro
Isobutylene Series With Amines and Ammonia

B2010
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B003/B066

nucleophilic agents in two ways according to the following scheme:



Whether this reaction proceeds according to 1 or 2, depends on the character of the olefin as well as on the attacking reagent. Under the action of anhydrous NH_3 the reaction takes place in all perfluoro isobutylenes investigated. 1-alkyl- and 1-aryl perfluoro isobutylenes react with secondary amines according to Scheme 2. The action of excess NH_4OH eliminates fluorine completely. There are 5 references: 2 Soviet, 1 German, 1 American, and 1 Canadian.

Card 2/3

Reactions of Fluoro-olefins. 11th Report.
Interaction of Compounds of the Perfluoro
Isobutylene Series With Amines and Anions

82040
S/062/60/000/02/03/012
B003/B066

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the
Academy of Sciences USSR)

SUBMITTED: July 4, 1958

X

Card 3/3

DYATKIN, B. L.

82041
S/062/60/000/02/04/012
B003/B066

5.3600

AUTHORS:

Knunyants, I. L., Dyatkin, B. L., German, L. S.,
Mochalina, Ye. P.

TITLE:

Reactions of Fluoro-olefins. 12th Report. Interactions of
Polyfluoro-chloro Butenes With Alcohols

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 2, pp. 231 - 236

TEXT: The authors investigate the action of sodium methylate and ethylate on linear dimers of 1,2-difluoro-1,2-dichloro ethylene and trifluoro-chloro ethylene. The experiment is described in detail in the experimental part of the paper. The structure was clarified by means of infrared spectrography. The investigations revealed that the reaction of 1,2,3,4-tetrafluoro-1,3,4,4-tetrachloro butene-1 with the alcoholates mentioned yields 1,1,1-trialkoxy-2,3,4-trifluoro-4,4-dichloro butene-2. When treating the linear dimer of trifluoro-chloro ethylene with the alcoholates, 3-alkoxy-4-chloro-perfluoro butene-1 results. The linear dimer of trifluoro-chloro ethylene was identified to be a mixture of

Card 1/2

15.8160

25481
S/020/61/139/001/013/018
B103/B226

AUTHORS: Dyatkin, B. L., Mochalina, Ye. P., and Knunyants, I. L.,
Academician

TITLE: Condensation of formaldehyde with perfluoro olefines -
tetrafluoro ethylene, hexafluoro propylene, and trifluoro
chloroethylene

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 1, 1961, 106-109

TEXT: The authors continued the investigation of chlorosulfonic acid as a catalyst of H. Prins' reaction (Ref. 1: Rec. trav. chim., 51, 469 (1932)) and endeavored to use this acid when extending the Prins reaction to perfluoro olefines: tetrafluoro ethylene, hexafluoro propylene, and trifluoro chloroethylene, in their interaction with formaldehyde. As is known, the Prins reaction belongs to the typical reactions of hydrocarbon olefines with electrophile reagents; especially, in this case, the condensation with formaldehyde in the presence of strong acids is meant. Such reactions are very difficult and, therefore, little investigated. The authors demonstrated by means of 1,2-difluoro-1,2-dichloro ethylene that

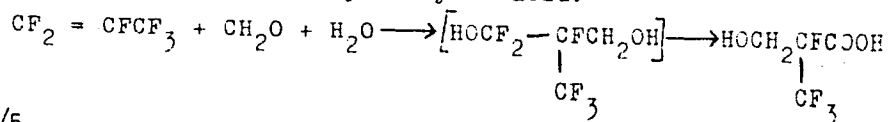
Card 1/5

25481

S/020/61/139/001/013/018
B103/B226

Condensation of formaldehyde...

both chlorosulfonic and fluorosulfonic acid are in this case highly effective catalysts of the Prins reaction, while H_2SO_4 of various concentrations could not release this reaction (I. L. Knunyants et al. Ref. 5: Zhurn. Vsesoyuzn. khim. obsch. im. Mendeleeva, c. 114 (1961)). It has been proved that a mixture of tetrafluoro ethylene $CF_2 = CFCl$, paraformaldehyde, and chlorosulfonic acid, heated up to $100^\circ C$. is subject to a condensation according to the general scheme of the Prins reaction, and yields α, α -difluoro hydracrylic acid which is isolated as its ethyl ester. As the yield of this ester was 61.6 %, the authors were of the opinion that chlorosulfonic acid is much more active than H_2SO_4 . The condensation of paraformaldehyde with hexafluoro propylene leads in the presence of chlorosulfonic acid at $130 - 150^\circ C$ to a 41-% yield of α -fluoro- α -trifluoro methyl hydracrylic acid:



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B103/B226

Condensation of formaldehyde...

The formation of this acid is in accord with the polarization of the double bond in hexafluoro propylene $\overset{\delta+}{\text{CF}}_2 = \overset{\delta-}{\text{CF}}-\text{CF}_3$. The double bond in $\text{CF}_2 = \text{CFCl}$ is polarized such that a partly negative charge is present on the carbon atom of the CFCl group. This has been repeatedly confirmed by reactions of nucleophile additions to $\text{CF}_2 = \text{CFCl}$. In the final result only derivatives of fluoroacetic acid are produced. Thus, the condensation of formaldehyde with trifluoro chloroethylene could be expected to lead to α -fluoro- α -chloro hydracrylic acid: $\text{HOCH}_2^+ + \overset{\delta-}{\text{CF}}_2 + \overset{\delta+}{\text{CFCl}} = \text{CF}_2 \longrightarrow [\text{HOCH}_2\overset{+}{\text{CFClCF}}_2] \xrightarrow{\text{H}_2\text{O}} \text{HOCH}_2\text{CFClCOOH}$.

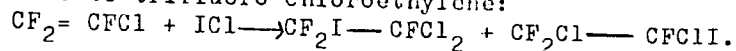
This acid has actually been isolated as its ethyl ester. The yield amounted to 19.8 % of the theoretical one. However, beside this yield, another 30.5 % of ethyl ester of α, α -difluoro hydracrylic acid have been produced. Its formation can be only explained as a result of the electrophile attack to the CF_2 group, i.e., to a negatively polarized carbon atom being more weak than is the case with the C atom in the CFCl group of trifluoro chloroethylene. I. L. Knunyants, V. V. Shokina and Li Chih-yüan (Ref. 9: DAN, Card 3/5)

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S/020/61/139/001/013/018
B103/B226

Condensation of formaldehyde...

136, 611 (1961)) observed two types of orientation in the addition of iodine chloride to trifluoro chloroethylene:



It could not be found out whether this reaction is released by the ionic or by the radical mechanism. However, in the condensation with formaldehyde, an orientation being opposed to polarity appears in a pronounced ionic process, viz., that of the electrophile addition to the double bond. The authors try to explain this phenomenon by the competition of the polar and steric factors. The effective radius of F is 1.25 Å, that of Cl 1.58 Å. Thus, the orientation of reaction which corresponds to polarity meets a great steric hindrance. The steric and polar factors, however, agree as to their effect in the nucleophile addition to trifluoro chloroethylene. Due to this fact, orientation in these reactions has to be a rigorously unambiguous one. There are 9 references: 2 Soviet-bloc and 7 non-Soviet-bloc. The three references to English-language publications read as follows: M. S. Raasch. (Ref. 2: Am. pat. 2452791); D. D. Coffman et al. (Ref. 3: J. Org. Chem. 14, 747 (1949)); E. T. McBee et al. (Ref. 4: J. Am. Chem. Soc., 74, 444 (1952)).

Card 4/5

Condensation of formaldehyde...

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S/020/61/135/001/013/018
B103/B226

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the
Academy of Sciences USSR)

SUBMITTED: March 23, 1961

Card 5/5

KNUNYANTS, I.L.; GERMAN, L.S.; DYATKIN, B.L.

α -Bromoperfluoroisobutyric acid and its derivatives. Izv.
AN SSSR. Otd.khim.nauk no.8:1513-1514 Ag '61. (MIRA 14:8)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Isobutyric acid)

KNUNYANTS, I.L.; GERMAN, L.S.; DYATKIN, B.L.; MOCHALINA, Ye.P.

Condensation of 1,2-difluoro-1,2-dichloroethylene with formaldehyde.
Zhur.VKHO 6 no.1:114 '61. (MIRA 14:3)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR.
(Ethylene) (Formaldehyde)

DYATKIN, B.L.; MOCHALINA, Ye.P.; KNUNYANTS, I.L., akademik

Condensation of formaldehyde with perfluorinated olefins:
tetrafluoroethylene, hexafluoropropylene, and trifluoroeth-
ylene. Dokl. AN SSSR 139 no.1:106-109 J1 '61. (MIRA 14:7)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Ethylene) (Formaldehyde)

KNUNYANTS, I.L.; DYATKIN, B.L.

Reaction of hexafluoroacetone with olefins. Izv. AN SSSR
Otd.khim.nauk no.2:355-356 F '62. (MIRA 15:2)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Acetone)
(Olefins)

39794

S/062/62/000/008/014/016
B101/B180

11.771↓
AUTHORS:

Knunyants, I. L., Dyatkin, B. L., and Mochalina, Ye. P.

TITLE:

Anionotropic rearrangement in reactions of perfluorobutadiene

PERIODICAL:

Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 8, 1962, 1483-1484

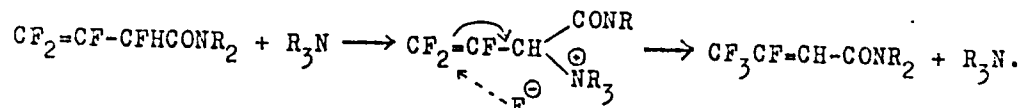
TEXT: The addition of nucleophilic reagents (e.g. alcohol) to hexafluorobutadiene-1,3 in the presence of triethylamine was investigated at 80°C. As oxidation of the addition compound with permanganate gives trifluoroacetic acid, while hydrolysis with H₂SO₄ gives trifluoroacetone, it is assumed that the primary addition occurs in the 1,2 position, and that the presence of the triethylamine causes an allyl rearrangement: $\text{CF}_2\text{-CF-CFHC}_2\text{OR} \rightarrow \text{CF}_3\text{CF-CHCF}_2\text{OR}$. This was proved in that the dialkylamides of α-hydroperfluorocrotonic acid (II) were obtained from the dialkylamides of α-hydroperfluorovinylacetic acid in the presence of triethylamine, as was the diethylamide of (II): b.p. 81-82°C/7 mm Hg; n_D^{20} 1.3983; d_4^{20} 1.2010. Oxidation of this product with KMnO₄ gave tri-

Card 1/2

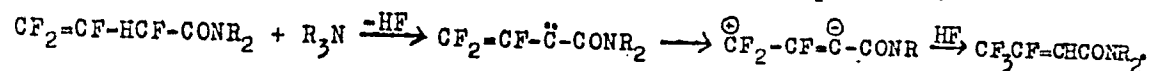
Anionotropic rearrangement in ...

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B101/B180

fluoroacetic acid in quantitative yield, and its hydrolysis with H_2SO_4 gave trifluoroacetone. Since neither anhydrous HF nor triethylaminefluorohydrate cause a rearrangement of the dialkylamine of (I) into the corresponding compound of (II), the triethylamine is assumed to have a specific effect:



The formation of a carben as an intermediate is also possible:



ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental Organic Compounds of the
Academy of Sciences USSR)

SUBMITTED: February 19, 1962

Card 2/2

KNUNYANTS, I.L.; DYATKIN, B.L.; GERMAN, L.S.; MOCHALINA, Ye.P.

Condensation of formaldehyde with trifluoroethylene. Izv. AN SSSR. Otd.
khim. nauk no. 9:1674-1677 S '62. (MIRA 15:10)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.,
(Formaldehyde) (Ethylene) (Chlorine compounds)

KNUNYANTS, I. L.; FOKIN, A. V.; DYATKIN, B. L.; KOMAROV, V. A.

Action of nitrogen dioxide on perfluoroisobutylene. Zhur.
VKHO 8 no.2:239-240 '63. (MIRA 16:4)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

(Nitrogen oxides) (Propene)

KHINYANTS, I.L.; DYATKIN, B.I.

Perfluoro tert-butyl alcohol and dissociation constants of
trifluoromethylcarbinols. Izv. AN SSSR, Seriya, no. 5-1964,
925 My 1964. (KIRA 1964)

1. Institut elementorganicheskikh soedineniy AN SSSR.

DYATKIN, B.L.; MOCHALINA, Ye.P.

Fluoroaliphatic diazo compounds. Report No.1: Some new
reactions of trifluorodiazethane. Izv. AN SSSR Ser. khim.
no.7:1225-1229 J1 '64. (MIRA 17:8)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

KNUNYANTS, I.L.; DYATKIN, B.L.; FOKIN, A.V.; KOMAROV, V.A.

Nitration of perfluoroisobutylene. Izv. AN SSSR. Ser. khim.
no.8:1425-1429 Ag '64. (MIRA 17:9)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

L 21735-65 EWT(m)/EPF(c)/EPR/EMP(j) Po-L/Pr-L/Ps-L SSD(a)/RPL RM/WW

ACCESSION NR: AP4044703

S/0062/64/000/008/1425/1429

AUTHOR: Knunyants, I. L.; Dyatkin, B. L.; Fokin, A. V.; Komarov, V. A.

TITLE: Nitration of perfluoroisobutylene

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 8, 1964, 1425-1429

TOPIC TAGS: perfluoroisobutylene, nitration, nitrogen tetroxide reaction, nitroperfluorobutylnitrite, perfluoroisobutyldinitrite, nitroperfluorobutanol, bistrifluoromethylglycolic acid

ABSTRACT: Perfluoroisobutylene was heated with an equimolecular amount of nitrogen tetroxide in an autoclave at 170-180C for 6-8 hours to attain nearly complete conversion. The reaction mixture was separated into two fractions: a fraction boiling 101-110C, and a fraction boiling 30-100C, apparently a mixture of perfluoroisobutyl- α, β -dinitrite, $(CF_3)_2C(ONO)CF_2ONO$, and its conversion products with nitrogen. Hydrolysis of the 30-100C fraction gave bistrifluoromethylglycolic acid (IX) in 27% yield based on initial perfluoroisobutylene. Nitroperfluoro-

cc:J/3

L 21735-65

ACCESSION NR: AP4041703

tert-butanol (IX) was obtained in 23% yield, based on initial perfluoroisobutylene, /
analysis of VI. No dinitro compound $(CF_3)_2C(NO_2)CFNO_2$ nor nitronitrite
 CF_3ONO , nor products which could be obtained by their conversion
were found, contrary to earlier data by I. L. Khunyanis and A. V. Fakin
(AN SSSR 111, 1035 (1956)). Orig. art. has: 7 equations and 10 formulae

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Organometallic Compounds, Academy of Sciences, SSSR)

SUBMITTED: 28Dec62

ENCL: 01

SUB CODE: GC, MT

NO REF SOV: 005

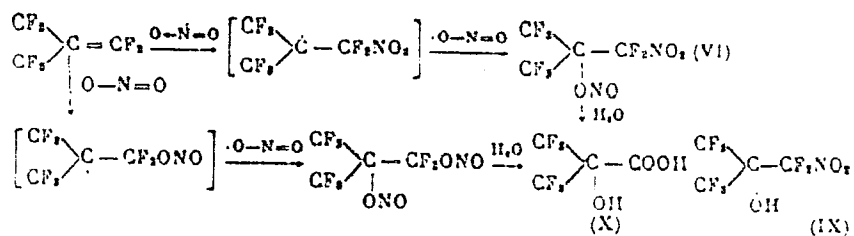
OTHER: 004

2/3

L 21735-65

ACCESSION NR: AP4044703

ENCLOSURE: 01



Card 3/3

MOCHALINA, Ye.P.; DYATKIN, B.L.

' Synthesis of 2-diazoperfluoropropane (bistrifluoromethyl-
azomethane. Izv. AN SSSR. Ser. khim. no.5:926-928 '65. (MIRA 18:5)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

DYATKIN, B.L.; MOCHALINA, Ye.P.

Fluoroaliphatic diazo compounds. Report No.2: α -Diazoperfluoro ketones. Izv. AN SSSR. Ser. khim. no.6:1035-1039 '65.

(MIRA 18:6)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

KNOX, J. L.; DEAN, E. L.; HENNING, J. L.

Perfluoro tert-butylamine. Izv. Akad. Nauk SSSR, Ser. Khim. 1965, 12:6

1. Institut elementoorganicheskikh soedineniy AN SSSR.

DYATKIN, B.I.; BEKKER, R.A.; FROSTAYTS, I.I.

Nitrosation of alkyl perfluorovinyl ethers. Izv. AN SSSR. Ser.
Khim. no.6:1121 '65. (MIRA 18:6)

1. Institut elementoorganicheskikh soedineniy AN SSSR.

GEVORKYAN, A.A.; DYATKIN, B.L.; KNUNYANTS, I.L.

Action of phosphoric acid esters on α -chloroperfluoronitroso
alkanes. Izv. AN SSSR. Ser. khim. no.9:1599-1606 '65.
(MIRA 18:9)

1. Institut elementoorganicheskikh soedineniy AN SSSR.

DYATKIN, B.L.; MOCHALINA, Ye.P.; KNUNYANTS, I.L.

Oxidation of hexafluoroacetone oxime in anhydrous hydrogen
fluoride. Izv. AN SSSR. Ser. khim. no.9:1715-1716 '65.
(MIRA 18:9)

1. Institut elementoorganicheskikh soedineniy AN SSSR.

DYATEKIN, P.L.; GEL'BYAN, A.A.; KNEBYANES, I.L.

Substitution of nitroso group in perfluorinated alkanes.
Izv. AN S.S.R. Ser. Khim. no. 10:1873-1875 1965.

(MIRA 18:10)

I. Institut elementoorganicheskikh soedineniy AN USSR.

DIATKIN, B.L.; MOCHALINA, Ye.P.; LANTSEVA, I.T.; KNUNYANTS, I.L.

Hexafluoroisobutyric acid in the Borodin-Hunsdiecker reaction.
Zhur.VKHO 10 no.4:469-470 '65.

(MIRA 18:11)

1. Institut elementoorganicheskikh soedineniy AN SSSR.

KNUNYANTS, I.I.; BYKHOVSKAYA, E.G.; DYATKIN, B.L.; FROSIN, V.N.;
GEVORKYAN, A.A.

Interaction of trifluoronitroisomethane and tert-perfluoro-
nitroisobutane with acid phosphites. Zhur.VKHO 10 no.4:472-
473 '65. (MIRA 18:11)

GEVORKYAN, A.A.; DYATKIN, B.L.; KHUMYANTS, I.I.

Certain reactions of tert-nitrosoperfluoroisobutane. Zhur. VKHO
10 no. 6:707-708 '65 (MIRA 19:1)

1. Institut elementoorganicheskikh soedineniy AN SSSR. Submitted July 22, 1965.

DYATKIN, B.L.; BEKKER, R.A.; KONNYANTS, I.L., akademik

Reaction of alkylperfluorovinyl ethers with nitrogen dioxide.
Esters of nitroperfluorocarboxylic acids. Dokl. AN SSSR 166
no.1:106-109 Ja '66. (MIRA 19:1)

1. Institut elementoorganicheskikh soedineniy AN SSSR. Submitted July 9, 1965.

KNUNYANTS, I.L.; SYATKIN, B.L.; MOCHALINA, Ye.P.; LANTSEVA, L.T.

Hexafluoroisopropylhydroxylamine and the dissociation constants
of some fluorinated hydroxylamines and oximes. Izv. AN SSSR. Ser.
khim. no.1:179-180 '66. (MIRA 19:1)

I. Institut elementoorganicheskikh soedineniy AN SSSR. Submitted
May 26, 1965.

L 31885-66 EWT(m)/ENP(j)/T WW/JW/JWD/RM

ACC NR: AP6012539

SOURCE CODE: UR/0062/66/000/003/0585/0585

AUTHOR: Dyatkin, B. L.; Mochalina, Ye. P.; Bekker, R. A.; Knunyants, I. L. 44
43
6

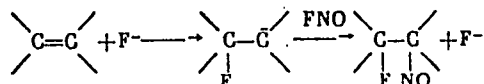
ORG: Institute of Elemental Organic Compounds, Academy of Sciences SSSR (Institut elementarnoorganicheskikh soyedineniy Akademii nauk SSSR)

TITLE: Mechanism of addition of nitrosyl fluoride to fluoroolefins

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 3, 1966, 585

TOPIC TAGS: organic synthesis, fluorine compound

ABSTRACT: The authors obtained experimental proof of the nucleophilic mechanism of addition of FNO to higher fluoroolefins. It was shown that alkali metal fluorides (especially in strongly ionizing media) are effective catalysts of this reaction



Perfluoroethylene reacts with FNO only at 120-150°C and the reaction of perfluoroethylene (15 g), FNO (5.5 g), CsF (2 g) and KF (4 g) produces 2-nitrosoperfluoropro-

Card 1/2

UDC: 541.124 + 546.16

L 31885-66

ACC NR: AP6012539

pane (14.3 g). Perfluorocyclobutene according to our observations does not react with FNO even during heating to 120°C; however, shaking of 8 g of perfluorocyclobutene, 4.5 g of FNO, 1 g CSF and 2 kg KF with 5 ml of tetramethylene sulfone at 35° for 3 hrs produces nitrosoperfluorocyclobutane with 70% yield.

SUB CODE: 07/ SUBM DATE: 30Dec65/ ORIG REF: 1002/ OTH REF: 001

LG

Card 2/2

05104-07 EWT(m)/EWP(j) JW/RM
ACC NR: AP7000738

SOURCE CODE: UR/0062/66/000/006/1124/1124

KNUNYANIS, I. L., DYATKIN, B. L., BEKKER, R. A., Institute of Heteroorganic
Compounds, Academy of Sciences USSR (Institut elementoorganicheskikh soedineniy
AN SSSR)

"New Method of Synthesizing Alpha-Difluoroaminoperfluorocarboxylic Acids and
Their Derivatives"

Moscow, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No 6, 1966, p 1124

Abstract: A new method of synthesizing alpha-difluoroaminoperfluorocarboxylic
acids and their derivatives on the basis of readily available alkylperfluorovinyl
ethers and tetrafluorohydrazine was discovered. The alkylperfluorovinyl ether
was treated with tetrafluorohydrazine, the adduct then treated with antimony
pentafluoride, and the $\text{RCF}(\text{NF}_2)\text{COF}$ formed quantitatively converted to esters of
alpha-difluoroaminoperfluoropropionic acid by treatment with alcohols. Orig. art.
has: 2 formulas. [JPRS: 37,023]

TOPIC TAGS: organic synthetic process, fluorocarboxylic acid, ether, vinyl compound
hydrazine, nonmetallic organic derivative

SUB CODE: 07 / SUBM DATE: 07Apr66 / OTH REF: 001

Card 1/1 vmb

UDC: 542.91 + 547.466 + 546.16

0923 1907

ACC NR: AP6032590

SOURCE CODE: UR/0062/66/000/008/1377/1382

AUTHOR: Knunyants, I. L.; Dyatkin, B. L.; Govorkyan, A. A.

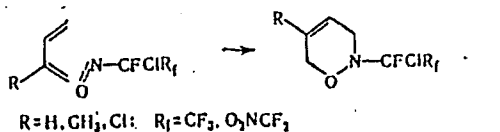
ORG: Institute of Organometallic Compounds, Academy of Sciences, SSSR (Institut olomentoorganicheskikh soyedineniy Akademii nauk SSSR)

TITLE: Reactions of α -chloroperfluoronitrosoalkanes with unsaturated compounds

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 8, 1966, 1377-1382

TOPIC TAGS: organic nitroso compound, fluorinated organic compound

ABSTRACT: The reactions of diene hydrocarbons and olefins (isobutylene and propylene) with two α -chloroperfluoronitrosoalkanes, α -chloroperfluoronitrosoethane CF_3CFCINO (I) and α -chloro- β -nitroperfluoronitrosoethane $\text{O}_2\text{NCF}_2\text{CFCINO}$ (II), are described. (I) and (II) reacted very readily in ether solution at -20 to -15°C with butadiene, isoprene and chloroprene. The main direction of the reaction is a diene-synthesis-type addition forming derivatives of 3,6-dihydro-1,2-oxazine:



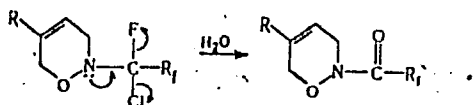
These compounds are unstable and darken rapidly at room temperature. They readily

Card 1/3

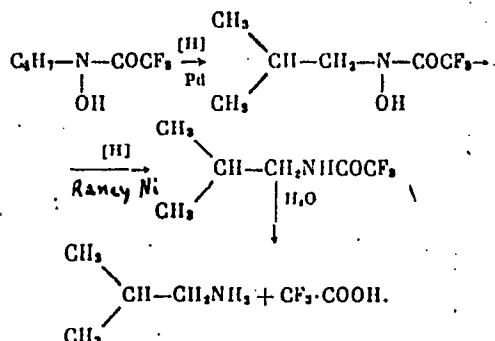
UDC: 542.91+547.231+661.723-16

ACC NR: AP6032590

hydrolyze to the corresponding stable perfluoroacyl derivatives



(I) and (II) also react very readily with isobutylene and propylene. Alkenyltrifluoroacetohydroxamic acid obtained from (I) and isobutylene was made to undergo the following reactions:



It is shown that the reactions of α -chloroperfluoronitrosoalkanes with isobutylene and propylene lead to the corresponding oxazethidines, whose hydrolysis yields N-(methal-

Card 2/3

ACC NR: AP6032590

lyl)perfluorohydroxamic and N-(allyl)perfluorohydroxamic acid Orig. art. has: 2
figures.

SUB CODE: 07/ SUBM DATE: 11Mar64/ ORIG REF: 007/ OTH REF: 006

Card 3/3

ACC NR: AP7004582

SOURCE CODE: UR/0020/66/168/006/1319/1322

AUTHOR: Dyatkin, B. L.; Bakker, R. A.; Knunyants, I. L. (Academician)

ORG: Institute of Heteroorganic Compounds, AN SSSR (Institut elementoorganicheskikh soyedineniy AN SSSR)

TITLE: Interaction of nitryl fluoride with alkylperfluorovinyl ethers. | Synthesis of esters of alpha-nitroperfluorocarboxylic acids

SOURCE: AN SSSR. Doklady, v. 168, no. 6, 1966, 1319-1322

TOPIC TAGS: fluorinated organic compound, vinyl compound, ether

ABSTRACT: Two alternative reaction schemes are described for the reaction of alkylperfluorovinyl ethers with nitryl fluoride: addition of FNO_2 at the double bond according to the polarity of the reagents (scheme 1), and production of alkoxyperfluoronitrosoalkanes (scheme 2). Alkyltri-fluorovinyl ethers react chiefly according to scheme 2, the formed nitroso-compound reacting with excess vinyl ether to oxazetidines. Alkyl-beta-chlorodifluorovinyl ethers and alkylperfluoropropenyl ethers react chiefly according to scheme 1. Ethylperfluoroisobutenyl ether reacts with nitryl fluoride in a stainless steel autoclave, yielding only a nitroso-ether; in an autoclave entirely lined with teflon, nitrofluorination accompanies the formation of the nitroso-compound. The reactions of nitryl chloride with alkylperfluorovinyl ethers were compared with those of nitryl fluoride. Nitryl chloride was found to behave similar to nitryl fluoride with respect to alkyltrifluorovinyl ethers; with alkyl-beta-chlorodifluoro-vinyl and alkylperfluoropropenyl ethers, exclusively chlorination products were obtained. Alkoxyperfluoronitrosoalkanes were also produced by oxidation

Card 1/2

UDC: 547.26'221.222.231.232

ACC NR: AP7004582

of the corresponding alkoxyperfluoronitrosoalkanes with nitrogen dioxide. Alkoxyperfluoronitrosoalkanes were readily converted to esters of alpha-nitroperfluorocarboxylic acids by reaction with anhydrous aluminum chloride, followed by treatment with ethanol. Esters of alpha-nitroperfluoropropionic acid were also formed by oxidation of esters of alpha-nitrosoperfluoropropionic acid by nitrogen dioxide. Properties of the ethyl ester of alpha-nitroperfluoropropionic acid were studied: it reacts with hydrogen chloride, yielding alpha-chloroper-fluoronitrosoethane; under the action of ammonia, it decomposes to alpha-hydroperfluoronitroethane and ethyl carbamate. Orig. art. has: 2 formulas and 1 table. [JPRS: 38,967]

SUB CODE: 07 / SUBM DATE: 02Dec65 / ORIG REF: 010 / OTH REF: 003

Card 2/2

ACC NR: AP7010719

SOURCE CODE: UR/0062/66/000/012/2247/2248

AUTHOR: Mochalina, Ye. P.; Dyatkin, B. L.; Knunyants, I. L.

ORG: Institute of heteroorganic compounds, Academy of Sciences USSR
(Institut elementoorganicheskikh sovediniy AN SSSR)

TITLE: Fluorine-containing phosphazo-compounds

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 12, 1966, 2247-2248

TOPIC TAGS: organic nitrogen compound, organic phosphorus compound,
fluorinated organic compound

SUB CODE: 07

ABSTRACT: It was found that fluorine-containing phosphazo-compounds may be prepared by reaction triphenylphosphine and triethylphosphite with tertiary perfluoronitrosoalkanes, in 75 and 68% yield, respectively. The reaction products were characterized. The first case of the formation of phosphazo compounds from perfluoronitrosoalkanes and derivatives of trivalent phosphorus was reported in 1965 at the laboratory of the authors. Orig. art. has: 2 formulas. [JPRS: 40,351]

Card 1/1

INDC: 567.221 1 661 710 1

ACC NR: AP0625994

SOURCE CODE: UR/0079/66/036/007/1326/1330

AUTHOR: Dyatkin, B. L.; Gevorkyan, A. A.; Khunyants, I. L.

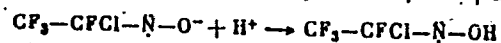
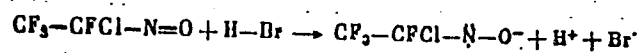
ORG: none

TITLE: Derivatives of trifluoroacetohydroxamic acid

SOURCE: Zhurnal obshchey khimii, v. 36. no. 7, 1966, 1326-1330

TOPIC TAGS: trifluoroacetohydroxamic acid derivative, chlorination, bromination, *FLUORINE COMPOUND, ACETAL, ORGANIC NITROSO COMPOUND, HALIDE, AMIDE*

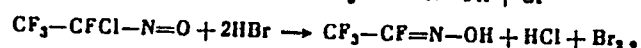
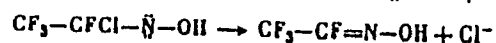
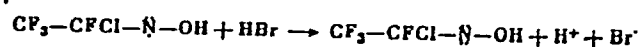
ABSTRACT: Hydrogenation of $\text{CF}_3\text{CF}_2\text{NO}_2$ over palladium black in absolute ether at an initial pressure of 120 atm gave $\text{CF}_3\text{CF:NOH}$ (bp $30-31^\circ\text{C}$, n_D^{20} 1.3230, d_{20} 1.1520), which was chlorinated at -40°C in tetrachloroethane in the presence of pyridine to form (92%) $\text{CF}_3\text{CFCIN:O}$. The latter was mixed with phenol and ethyl ether at -78°C and then brominated with HBr at -30°C to form $\text{CF}_3\text{CF:NOH}$, which was identified as $\text{CF}_3\text{CF:NOH} \cdot 0.5(\text{C}_2\text{H}_5)_2\text{O}$ (bp $78-80^\circ\text{C}$, n_D^{20} 1.3245, d_{20} 1.1200):



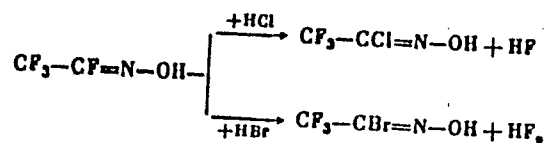
Card 1/3

UDC: 547.413.5

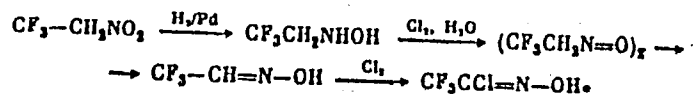
ACC NR: AP6025994



In this reaction, F may be substituted either by Cl (which is formed during the reaction) or by Br, when the reaction is conducted with an excess of HBr, to form $\text{CF}_3\text{CCl:NOH}$, identified as $\text{CF}_3\text{CCl:NOH} \cdot 0.5(\text{C}_2\text{H}_5)_2\text{O}$ (bp 48°C , n_D^{20} 1.3610, d_4^{20} 1.2440) and $\text{CF}_3\text{CBr:NOH}$, identified as $\text{CF}_3\text{CBr:NOH} \cdot 0.5(\text{C}_2\text{H}_5)_2\text{O}$ (bp $60-61^\circ\text{C}$, n_D^{20} 1.3870, d_4^{20} 1.5170):



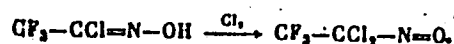
Chlorination of an aqueous solution of $\text{CF}_3\text{CH}_2\text{NHOH}$ yielded a blue nitroso compound which dimerized to $(\text{CF}_3\text{CH}_2\text{NO})_2$, mp $82.5-83.5^\circ\text{C}$; this when chlorinated at -20°C in HCl yielded (55%) $\text{CF}_3\text{CCl:NOH}$, bp $98-102^\circ\text{C}$, n_D^{20} 1.3610.



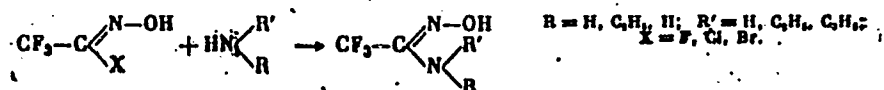
Card 2/3

ACC NR:AP6025994

$\text{CF}_3\text{CCl}_2\text{NOH}$ in mixtures with pyridine and Cl (mixed at -40°C) on warming to room temperature yielded $\text{CF}_3\text{CCl}_2\text{N:O}$, bp 36°C , n_D^{20} 1.3350, d_4^{20} 1.5020.



The above trifluoroacetoxyhydroxamic acid halides react with NH_3 and amines to form the corresponding amides:



By this reaction, $\text{CF}_3\text{C}(\text{:NOH})\text{NH}_2$, bp 62°C , n_D^{20} 1.3950, d_4^{20} 1.5640; $\text{C}_6\text{H}_5\text{C}(\text{:NOH})\text{NH}_2$, bp $57-58^\circ\text{C}$, n_D^{20} 1.4149, d_4^{20} 1.1960; and the anilide $\text{C}_6\text{H}_5\text{C}(\text{:NOH})\text{NH}_2$, mp $70.5-71.5^\circ\text{C}$, bp $98-100^\circ\text{C}$ were obtained.

[PS]

[WA-50; CBE No. 14]

SUB CODE: 07/ SUBM DATE: 16Jun65/ ORIG REF: 005/ OTH REF: 002

Card 3/3

ACC NR: AP0032278

SOURCE CODE: UR/0020/66/170/002/0337/0339

AUTHOR: Knunyants, I. L. (Academician); Dyatkin, B. L.; Bekker, R. A.

ORG: Institute of Heteroorganic Chemistry, Academy of Sciences, SSSR (Institut elementoorganicheskoy khimii Akademii nauk SSSR)

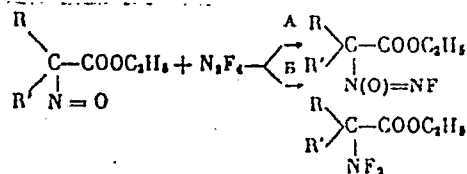
TITLE: Reactions of tetrafluorohydrazine with alpha-nitrosoperfluorocarboxylic acid esters

SOURCE: AN SSSR. Doklady, v. 170, no. 2, 1966, 337-339

TOPIC TAGS: tetrafluorohydrazine reaction, nitrosoperfluorocarboxylic acid ester, ester, chemical reaction, organic nitroso compound, hydrazine compound, fluorohydrin, carboxylic acid

ABSTRACT: In an autoclave at 70-80°C, N_2F_4 reacts with ethyl esters of nitrosodifluoroacetic acid, nitrosochloroacetic acid, and alpha-nitrosoperfluoropropionic acid according to the reaction

A:



1) $\text{R}=\text{R}'=\text{F}$,

3) $\text{R}=\text{F}$, $\text{R}'=\text{CF}_3$,

2) $\text{R}=\text{F}$, $\text{R}'=\text{Cl}$,

4) $\text{R}=\text{R}'=\text{CF}_3$.

Card 1/2

UDC: 547.221.231.235

ACC NR: AP6032278

to form the corresponding esters shown in the table.

[WA-50; CBE No. 12]

Table 1.

Compound	yield, %	bp	n_D^{20}	d_4^{20}	MR _D		found, %				calculated, %			
					found	calculated	C	H	F	N	C	H	F	N
CF ₃ -COOC ₂ H ₅	32	50/30	1.3635	1.3755	30.77	30.11	26.16	2.69	31.20	14.88	23.81	2.71	30.63	15.05
N(O)=NF														
CFCl-COOC ₂ H ₅	21	54/12	1.4083	1.4061	35.50	35.59	23.55	2.53	19.14	13.75	23.72	2.49	18.81	13.85
N(O)=NP														
CF ₃ CF-COOC ₂ H ₅	35	81/33	1.3510	1.4351	35.67	34.18	25.55	2.09	40.17	11.85	25.43	2.13	40.24	11.84
N(O)=NF														
CF ₃ C-COOC ₂ H ₅ CF ₃ N(O)=NF	45	50/20	1.3490	1.5042	40.57	40.81	25.50	1.08	47.12	0.82	25.18	1.76	46.48	9.71
CF ₃ C-COOC ₂ H ₅ CF ₃ NF ₂	51	65/100	1.3230	1.4868	37.03	37.10	26.20	1.87	55.34	5.23	20.19	1.83	55.25	5.00

SUB CODE: 07/ SUBM DATE: 10Mar66/ ORIG REF: 006/ OTH REF: 004/

Cord 2/2

100 AND 1TH CROSS

1ST AND 2ND CROSS

PROCESSES AND PROPERTIES INDEX

25

DIATKIN, M. E.

Biradicals. (In Russian.) M. E. Diatkin and Ia. K. Syrkin. *Izvestiya Khimii* (Progress in Chemistry), v. 16, no. 1, 1947, p. 29-68.

The possibility of the existence of biradicals, tri-radicals, etc. (that is, the presence of two or more trivalent carbon atoms in one molecule) was investigated by means of a thorough study, using both chemical and magnetic methods on a series of organic compounds. A new theory of biradical compounds is advanced. 61 ref.

ASB-5LA METALLURGICAL LITERATURE CLASSIFICATION

REGIONAL DIVISION

1ST AND 2ND CROSS

100 AND 1TH CROSS

1ST AND 2ND ORDERS										3RD AND 4TH ORDERS									
PROCESSES AND PROPERTIES INDEX																			
<p><i>Handwritten: 41</i></p> <p><i>Handwritten: K</i></p> <p>Ionic character and dipole moments of bonds. M. E. Diatkina (<i>Acta Physicochim. U.R.S.S.</i>, 1940, 18, 639-646). On the basis of Wall's theory (A., 1940, 1, 244) dipole moments of the "transition" structures are calc. for a no. of compounds, and a physical interpretation of these structures is offered. Calculation of the wts. of the various structures offered. (Calculation of the wts. of the various structures offered for the NH_3 and shows that the Kassel structure ($\text{N}^+ \text{H}^- \text{H}^- \text{H}^-$) is insignificant, whilst the transition structures are of great importance. The dipole moment of homopolar structures is very small and may be ignored. F. L. U.)</p>																			
Sci. Res. Physico-Chemical Inst. im L. Ya. Karpov																			
<p>ASB. I.L.A. METALLURGICAL LITERATURE CLASSIFICATION</p> <p>1940-1949</p>																			

1ST AND 2ND SECTIONS		PROCESSING AND PROPERTIES INDEX	
<p><i>ca</i></p> <p>Resonance in organic chemistry. Ya. K. Syrkin, M. R. Dyakshin and A. A. Zhukhovitskii. <i>Uspekhi Khim.</i> 10, 121-57(1941), and Corrections, <i>Ibid.</i> 769. -- Review. Resonance and valence states of the individual atoms are discussed. The resonance structures of hydrocarbons and their derivs., orientation in the benzene and naphthalene rings, inductive effect and alternating polarity are considered. Chemical structures do not indicate the full possibilities of the reactions of org. compds. These can be found only by considering all possible polar as well as ionic structures, also the possibilities of hydrogen bonds, chelation, steric hindrance and valence strains. In considering the various resonance states the relative probability and the energy relations must be taken into account. In the case of reactions the thermodynamic and the kinetic factors must be distinguished, especially in the case of competitive reactions. A reinterpretation of Ingold's ideas completely in terms of quantum mechanics should lead to fruitful results.</p> <p>R. H. Rathmann</p>		<p>2</p>	
<p>ASAC-SLA METALLURGICAL LITERATURE CLASSIFICATION</p>			
<p>FROM SYMBIOTIC</p>		<p>FROM SYMBIOTIC</p>	
<p>SYMBOLS</p>		<p>SYMBOLS</p>	
<p>SYMBOLS</p>		<p>SYMBOLS</p>	

10

ca

The structure of the naphthalene molecule. Ya. K. Syrkin and M. E. Dyatkina, *Acta Physicochim. U. R. S. S. 14, 105-118(1941)* (in English).--Theoretical. The nos. of structures for given groups and their relative wts. are tabulated and from their consideration conclusions are drawn as to the relative reactivities of benzene, naphthalene, anthracene and more highly condensed ring systems.

P. H. Rathmann

ASD-11-A METALLURGICAL LITERATURE CLASSIFICATION

COMMON ELEMENTS		COMMON VARIANTS	
<p>Inductive effect. Ya. K. Syrkin and M. H. Dynskan. <i>Acta Physicochim. U. R. S. S.</i> 14, 185-92(1941).—The effect of substituents on the distribution of charges in org. compds. is treated as an effect of resonance with stabilized ionic structures. A quant. examn. of the energies of such structures is made for NPhMe, I and PhCl, and the directing influence of these substituents is shown to follow from the assumptions made. PhSO_2H, toluene and PhNO_2 are also discussed. B. C. P. A.</p>		2	
<p>ASR-51A METALLURGICAL LITERATURE CLASSIFICATION</p>			
<p>GROUPS</p>		<p>LETTERS</p>	
<p>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100</p>		<p>1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100</p>	

2A

2

Structure of boron hydrides. Ya. K. Syrkin and M. E. Dyatkina. *Acta Physicochim. U. R. S. S. 14, 547*.
 The proposed structure for B₁₀H₁₂ contains a B⁺ ion bonded with 4 H atoms and a B⁻ ion bonded with 2 H atoms; in the actual mol. resonance occurs between this and a corresponding structure with the signs reversed. Somewhat similar structures are suggested for the remaining hydrides; all of them contain trivalent B⁺ and quadrivalent B⁻ ions. B. C. P. A.

COMMON ELEMENTS

WATERGAS

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

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100 AND 101. SEVERAL
 PROPERTIES AND PROPERTIES, MPB

2

The ionic character of bonds and the polarity of molecules. H. M. B. Dzyalinskaya, *J. Phys. Chem.* (U. S. S. R.) 15, 807-14 (1941); cf. *C. A.* 36, 2189. — In continuation of the earlier work, the relative weights (importance) for the three bond types were calcd. for the halogen acids. The importance of the homopolar link rises in the series F, Cl, Br, I; the so-called transition structure is generally of greater weight than the ionic structure. Pauling (*The Nature of the Chemical Bond*) obtained different values for the weight of the ionic structure because of over-simplified calcn. and because of ignoring the moment of the transition structure. Calcn. for the C-halogen bond, shows a somewhat higher weight of the ionic structure and lower, and more const., weight of the transition structure for the halogen series. Calcns. of the structure weights were also made for: O-Me, N-Me, MeOH, MeO, MeNH₂, MeNH and Me₂N. For the O compds. there is a uniformly high weight of the transition form which substantially exceeds the ionic form; for these compds. the transition structures cannot be ignored. Calcns. for the HCl bond and for H₂S were also made. Compds., particularly those with multiple bonds, are discussed mathematically. Although the calcn. is an approximation, it is possible to assert that in propylene the ionic bond is negligible, as well as the transition form; but the small weight of these forms conditions the polarity of this molecule, aldn. of H halide, etc. Analysis of halogenated acetylenes shows that the transition forms have greater weight than do the ionic forms; in this resonance the structures with a pos. halogen atom are unimportant and the great lowering of the moment caused by them is due to the great polarity of these mols. because of large atomic distances between the pos. and neg. charges. G. M. Kinsoloff

A B C D E F G H I J K L M N O P Q R S T U V W X Y Z AA BB CC DD EE																									
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<p>10</p> <p>Concerning V. V. Razumovskii's "theory" of structure of organic compounds. M. E. Dyatkina. <i>J. Phys. Chem.</i> (U. S. S. R.) 15, 691 6 (1941). - A polemic article in which the theory of structure of org. compounds proposed by Razumovskii in a no. of U. S. S. R. publications (1930-40) is attacked as being inconsistent with known exper. facts.</p> <p>G. M. Kosolapoff</p>																									
<p>11</p> <p>12</p> <p>13</p> <p>14</p> <p>15</p> <p>16</p> <p>17</p> <p>18</p> <p>19</p> <p>20</p> <p>21</p> <p>22</p> <p>23</p> <p>24</p> <p>25</p> <p>26</p> <p>27</p> <p>28</p> <p>29</p> <p>30</p> <p>31</p> <p>32</p> <p>33</p> <p>34</p> <p>35</p> <p>36</p> <p>37</p> <p>38</p> <p>39</p> <p>40</p> <p>41</p> <p>42</p> <p>43</p> <p>44</p> <p>45</p> <p>46</p> <p>47</p> <p>48</p> <p>49</p> <p>50</p> <p>51</p> <p>52</p> <p>53</p> <p>54</p> <p>55</p> <p>56</p> <p>57</p> <p>58</p> <p>59</p> <p>60</p> <p>61</p> <p>62</p> <p>63</p> <p>64</p> <p>65</p> <p>66</p> <p>67</p> <p>68</p> <p>69</p> <p>70</p> <p>71</p> <p>72</p> <p>73</p> <p>74</p> <p>75</p> <p>76</p> <p>77</p> <p>78</p> <p>79</p> <p>80</p> <p>81</p> <p>82</p> <p>83</p> <p>84</p> <p>85</p> <p>86</p> <p>87</p> <p>88</p> <p>89</p> <p>90</p> <p>91</p> <p>92</p> <p>93</p> <p>94</p> <p>95</p> <p>96</p> <p>97</p> <p>98</p> <p>99</p> <p>100</p>																									

Structure of boron hydrides. M. E. Dautkina and J. V. V. (Compt. rend. Acad. Sci. U.R.S.S., 1942, **35**, 180-183) calculated diffraction intensity curves of B_2H_6 , calc. for the author (A., 1941, I, 401), compared with Bauer's data (A., 1935, I, 401), agree as well as do those given by Bauer's C_{2v} -like model for mol. dimensions 1.80 ± 0.04 , 1.23 ± 0.03 , and 1.33 ± 0.03 Å for $B-H$, $B-B$, and $B-H_{ext}$, and the angles $123 \pm 8^\circ$ and $93 \pm 3^\circ$ for $H-B-H_{ext}$ and $H-B-H_{int}$, respectively. L. J. J.

DIATELINA, M. Ye.; SYRKIN, Ya. K.

Physico-Chemical Institute imeni L. Ya. Karpev, Moscow (-1941-)

"On the Question Concerning the Structure of Boranes"
II Zhur. Fiz. Khim., Vol. 17, No. 1, 1943

BR-52059019

Pa

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REMARKS ON THE PAPER "APPLICATION OF RESONANCE TO ORGANIC CHEMISTRY" BY V. I. OSMITSEV, YA. K. SYRKIN, M. R. DYATKINA, AND A. A. ZHUKHOVITSKIĬ. *Vopr.* Khim. 13, 80-1 (1944); cf. C.A. 35, 7779; 38, 72²¹. Polemical. F. H. Rathmann

10

COMMON ELEMENTS
COMMON VARIABLE METALS

ASAC-SLA METALLURGICAL LITERATURE CLASSIFICATION

EXACTLY REPRODUCED
EXACTLY REPRODUCED

61. 161

Structure of complex compounds. I. J. Sirkin and M. Dvorkina (Acta Physicochim. U.R.S.S., 1945, 20, 137-160).—The energy levels of atoms with d electrons are compared for states with equal levels of unpaired electrons distributed in different ways over the d and s orbitals. In the elements Sc—Ni, the transition of one of the two paired s electrons into the d orbital decreases with increasing at no. to 0.6 kg.-cal. in the case of Ni. It is concluded from a discussion of the possibilities of unpairing of electrons in d , s , and p orbitals that the max. no. of electrons (n) which may participate in valency bonds is 9 ($5d + 1s + 3p$). For V, Cr, Mn, Fe, Co, and Ni, n is 6, 6, 7, 8, 9, and 9, respectively. The existence of these high valency states is supported by magnetic moments of Cr, Mn, Mn, Fe, Os, Co, Ni, Pt, Cu, and Au compounds. Structural formulae for metal carbonyls, nitrosyls, and NO_2 -compounds are proposed.

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CA

2

Formation of hybrid bond orbitals with unshared electron pairs and the structure of TeCl_4 . M. Dyatkina (Karpov Inst. Phys. Chem., Moscow). *Acta Physico-chem. U.R.S.S.* 20, 407-10(1945).—Formation of 4 covalent bonds with symmetry C_{2v} as in TeCl_4 , $(\text{C}_6\text{H}_5)_2\text{SeCl}_2$, and $(\text{C}_6\text{H}_5)_2\text{SbBr}$ may occur in electron configurations p^4 , d^{10} , d^8 , and d^6 and eliminates the assumption of formation of hybrid bond orbitals with unshared electron pairs in these compounds. H. S. van Klooster

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COMMON ELEMENTS

Interatomic distances and ionic character of bonds. M. Dyatkina (Karpov Inst. Phys. Chem., Moscow). *Acta Physicochim. U.R.S.S.* 20, 683-94 (1945). Tables are given of bond distances for halides and methods of 20 elements. Subtracting the covalent radius of C or N (halogen) from the observed distance in MX_n or MX_n gives the apparent covalent radius r_a for element M. For elements of groups 4, 5, and 6 of the periodic table, r_a is smaller for the halides than for the methods and decreases with decreasing at. wt. of the halogen. This shows that the distance decreases with increasing ionic character of the bond. For elements of groups 2 and 3, and for bivalent Sn and Pb, r_a is again smaller for halides than for methides, but increases with decreasing at. wt. of the halogen. This is due to the possibility of electron attachment into free orbitals of M, which allows contribution of structures $M^+ = X^-$, this contribution being greater the smaller the electronegativity of the halogen. A. O. Allen

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SECTION TWENTY FOUR HUNDRED THREE

COMMON ELEMENTS		COMMON VARIABLE WORDS	
<p>Energy of quinoid forms. A. J. Naiman, M. K. Dyna- hina, and Ya. K. Sytkin (Inst. Fine Chem. Technol., Moscow). <i>Compt. rend. acad. sci. U.R.S.S.</i> 68, 987-9 (1945).—The energy of <i>p</i>-(I) and <i>m</i>-quinodimethane (II) have not been isolated is attributed to their high reactivity. The ratio β/α coincides with values for other hydro- carbons, and amounts to 0.84 for both I and II. In the case of hypothetical <i>m</i>-quinodimethane (III), the energy was found equal to $C + 1.41\beta$, if all 14 excited structures are taken into account. This indicates that although III is much less stable than I and II, the <i>m</i>- quinoid form may be present in small quantities in mole- of the type of <i>m</i>-nitroaniline. Frank Copet</p>			
<p>is calc. by use of the Heitler-London-Slater-Pauling (HLSP) method (C.A. 27, 3877) and Hückel's method of mol. orbitals (C.A. 26, 5826). The latter method gave the following level values: $C = 2.19\beta$, $C = 1.30\beta$, $C =$ 1.19β, and $C = 0.30\beta$ for II; and $C = 2.17\beta$, $C = 1.48\beta$, $C = \beta$, and $C = 0.31\beta$ for I (where C and β stand for the coulombic and resonance integrals in Hückel's method). Results obtained by using both methods show that both I and II possess considerable energy. Superposition of all 14 structures results in a high resonance energy. The resonance energy values obtained by the HLSP method were 1.04α for II and 1.05α for I; by Hückel's method, 1.92β for II and 1.94β for I, where α is the coeff. of the exchange integral. The fact that the quinodimethanes</p>			
<p>ASB-51A METALLURGICAL LITERATURE CLASSIFICATION</p>			
FROM SYNONYM		FROM BOWLING	
SYNONYM NO.		BOWLING NO.	
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100		1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100	

[illegible]

PA 54T36

USSR/Chemistry - Quinones
Chemistry - Resonance, Energies

Sep/Oct 1946

"The Reduction Potentials of Quinones and Resonance Energy," M. Dyatkina, Ya. Syrkin, Karpov Inst Phys Chem, Moscow, 22 pp

"Acta Physicochimica URSS" Vol XXI, No 5

Reduction potentials of quinones are correlated with changes in resonance energy on passing over from the quinone to corresponding hydroquinone. Parallelism found between changes in resonance energy and reduction potentials. Data on resonance energy allow value to be predicted for potentials of uninvestigated quinones. Received, 15 Oct 1945.

54T36

Resonance energies of polynuclear hydrocarbons. J. R. Sirlin

and M. E. Mathias (Bull. Acad. Sci. U.R.S.S. Chem. 1946, 183-178).

New results of calculations by the mol. orbital method of the resonance energies of 70 hydrocarbons and free radicals, of supposedly planar configuration, are given in terms of β (17.2 kcal.), a resonance integral of two adjacent C atoms. From these data and those of Hückel and others certain rules governing changes of resonance energy within structural series, in isomerisation, and in addition reactions are enunciated, and miscellaneous topics, e.g., dissociation into free radicals, are discussed. (a) *Linear (acene) and angular (phenes) polynuclear hydrocarbons.* Phenenes have higher resonance energies than acenes with the same no. of benzene nuclei.

(cf. excitation energies to the triplet state, which are greater with phenenes than with acenes; A., 1946, 1, 199) and hence are more stable (cf. the Pries rule), e.g., (4 rings) 9:10-benzophenanthrene (7-24 β), 1:2-benzophenanthrene (7-20 β), and naphthalene (II) (6-94 β); (5 rings) 1:2,6:6-dibenzanthracene (8-92 β) and pent-phenene (II) (8-54 β). In the acene series the extra resonance energy for each benzene ring added decreases slightly, thus C₁₂H₈ (III) (8 β), C₁₄H₁₀ (IV) (3-68 β), C₁₆H₁₂ (V) (5-32 β), (II) (6-94 β), (III) (8-54 β), (IV) (10-128 β). (b) *Condensed rings.* Pyrene (6-66 β), perylene (6-66 β), coronene (VI) (10-64 β). The resonance energy of (VI) when calc. on one electron is 0-64 β and hence represents nearly half of graphite (0-88 β).

(c) *Conjugation of Ph rings.* The mol. orbital method gives for diphenyl (VII) a val. (4-38 β) which is 0-38 β above that of two (III) rings and supports the idea of conjugation. A further Ph group, whether in the o-, m-, or p- (VIII) position, gives a val. (6-76 β) representing the same increase (0-34 β) as that due to the first. A similar increase occurs with p-quaterphenyl (IX) (9-16 β), i.e., $-(4 \times 2\beta) + (3 \times 0-38\beta)$, and Wheland (A., 1934, 1, 1159) obtained the same val. for the m-isomer, s-C₁₈H₁₄ (X) (11-16 β). Thus, m- and p-polyphenyls with the same no. of C₆ rings have identical resonance energies.

Conjugation of non-adjacent rings would give additional structures with one extended bond in the m-compounds, but the calculations show that they have hardly any effect on the energy. The differences in optical behaviour (displacement of max. absorp. for longer λ with increase in the C₆ chain in the case of p-polyphenols—taken to indicate conjugation—and no displacement in the case of m-polyphenyls, found by Gillam and Hey (A., 1939, 2, 448) cannot, therefore, be explained on energy differences in the ground state; on the other hand, the energies of excitation from the singlet to the triplet state (A., 1946, 1, 199) are approx. the same for m-polyphenyls, e.g., m-terphenyl (1-32 β), m-quaterphenyl (1-32 β), p-quinquephenyl (1-42 β), p-sextiphenyl (0-96 β), so there may be some constancy between the optical changes and the excitation states. (d) *Double bonds.* One external CC bond (styrene 2-42 β , 1-12 β), 2-C₆H₄-CH=CH₂ (4-10 β) adds -0.62β to the resonance energy of (III) or (IV), and a second (1:2-C₆H₄-(CH=CH₂)₂ (9-16 β , i.e., $-(4 \times 2\beta) + (3 \times 0-38\beta)$), and Wheland (A., 1934, 1, 1159) obtained the same val. for the m-isomer, s-C₁₈H₁₄ (X) (11-16 β). Thus, m- and p-polyphenyls with the same no. of C₆ rings have conjugation across the ring has scarcely any effect, the excitation

3

Inclusion of hetero atoms in the molecular orbital method. A. Ya. Namiot and M. E. Dyatkina (Inst. Technol. Fine Chemicals, Moscow). *Compt. rend. acad. sci. U.R.S.S.*, 53, 809 (1960). It was found that in systems in which the hetero atoms are not replaced by atoms of C, but rather by centers with a stronger field (such as N or O), the coulomb energy of the electron is larger by a quantity denoted by δ when compared with that in the field of the C atom. The resonance energy as a function of the parameter δ was then detd. for different values of δ in β units for 12 different systems. A comparison of the results shows that the introduction of only one new parameter in the method of mol. orbits does not give a sufficient picture of the systems examd., and further work is still necessary.

H. P. Pool

ASB 55.4 METALLURGICAL LITERATURE CLASSIFICATION

CARD AND INDEX DESIGN	
PROCEDURES AND PROPERTIES NOTES	
C.A.	2
The coordination numbers five, seven, and eight. M. R. Dymkova. <i>Vysokhi Khim.</i> 15, 37-52(1948).—Re- view bearing on the less common valence coordination nos. in mole., mol. crystals, and complex compds., up to 1944. 50 references. N. Thou	
ASTM-A METALLURGICAL LITERATURE CLASSIFICATION	
15000 STYVIBLVN	15000 BOWIVU
140000 P.J.	15000 HAP GUY ECU
A V K O J I	E A I S U Q R T W X Y Z

DIATKINA, M.

The L. Ya. Karpov Physico-Chem. Inst., (-1946-).

"On the Problem of the Participation in the Hybridization of an
Unshared Electron Pair."

Zhur. Fiz. Khim., No. 4, 1946.

1ST AND 2ND GROUPS																										3RD AND 4TH GROUPS									
PROCESSES AND PROPERTIES INDEX																																			
<p>65. Structure of Complex Compounds, Part I, by Ya. K. Syrkin and M. E. Dyatkina. <u>ZHURNAL OSHCHEI KHIMII</u> 16, p. 342-378, 1946. Complex-forming atoms are distinguished by a small differences between the energy levels of the d, s, and p electrons, which make valencies of up to none possible. Structural formulae based on this assumption are advanced for ionic and non-ionic complexes of the type $[MR_x]$, where M is a metal, and R = CO, CN, NO, NO₂, or NH₃.</p>																																			
<p>ASB-1LA METALLURGICAL LITERATURE CLASSIFICATION</p>																																			
<p>1ST AND 2ND GROUPS 3RD AND 4TH GROUPS 5TH AND 6TH GROUPS 7TH AND 8TH GROUPS 9TH AND 10TH GROUPS 11TH AND 12TH GROUPS 13TH AND 14TH GROUPS 15TH AND 16TH GROUPS 17TH AND 18TH GROUPS 19TH AND 20TH GROUPS 21ST AND 22ND GROUPS 23RD AND 24TH GROUPS 25TH AND 26TH GROUPS 27TH AND 28TH GROUPS 29TH AND 30TH GROUPS 31ST AND 32ND GROUPS 33RD AND 34TH GROUPS 35TH AND 36TH GROUPS 37TH AND 38TH GROUPS 39TH AND 40TH GROUPS 41ST AND 42ND GROUPS 43RD AND 44TH GROUPS 45TH AND 46TH GROUPS 47TH AND 48TH GROUPS 49TH AND 50TH GROUPS 51ST AND 52ND GROUPS 53RD AND 54TH GROUPS 55TH AND 56TH GROUPS 57TH AND 58TH GROUPS 59TH AND 60TH GROUPS 61ST AND 62ND GROUPS 63RD AND 64TH GROUPS 65TH AND 66TH GROUPS 67TH AND 68TH GROUPS 69TH AND 70TH GROUPS 71ST AND 72ND GROUPS 73RD AND 74TH GROUPS 75TH AND 76TH GROUPS 77TH AND 78TH GROUPS 79TH AND 80TH GROUPS 81ST AND 82ND GROUPS 83RD AND 84TH GROUPS 85TH AND 86TH GROUPS 87TH AND 88TH GROUPS 89TH AND 90TH GROUPS 91ST AND 92ND GROUPS 93RD AND 94TH GROUPS 95TH AND 96TH GROUPS 97TH AND 98TH GROUPS 99TH AND 100TH GROUPS</p>																																			

DYATKINA, M. E.

PA 18T81

USSR/Chemistry - Valency
Chemistry - Affinity

Jun 1946

"Covalency Explanation of Pauling's Electrostatic
Valency Rule," M. E. Dyatkina, 1 p

"Zhur Fiz Khim" Vol XX, No 6

Offers covalency explanation of Pauling's rule by
using CuCl , SiO_2 and Cu_2O as example.

18T81

DYATKINA, M. Ye.

"Energies of Systems With Heteroatoms," Sub 19 May 47, Sci Res Order of the Labor
Red Banner Physicochemical Inst imeni L. Ya. Karpov.

Dr. Chem Sci
Dissertations presented for degrees in science and engineering in Moscow in 1947.

SO: Sum.No.457, 18 Apr 55

DYATKINA, M. YE.

USSR/Chemistry - Resonance
Chemistry - Isomerism

Nov 1947

"Energy Resonance of Open Chain with Heteroatoms at the Terminal Point of the Chain," M. Ye. Dyatkina, 4 pp

"Dok Ak Nauk" Vol LVIII, No 6

In a previous work, the author developed a method of molecular orbits in heterocyclic unions with nitrogen by means of calculations on: 1) the increased energy of the electron of the heteroatom, and 2) increased energy of the transfer interrelationship between the heteroatom and the carbon atom. In this article, the author discusses a like method for the study of the systems with heteroatoms at the end of the chains of doublets in such materials as unsaturated carbonyl unions. Submitted by Academician A. N. Frankin 16 Jun 1947.

3676

DYATKINA, M. E.

USSR/Chemistry - Systems
Chemistry - Nitrogen

Sep 1947

"Energies of Systems with Coupled Double Bonds and
Different Atoms," M. E. Dyatkina, 18 pp

"Zhur Fiziches Khim" Vol XXI, No 9, pp 989-1006.

A well-illustrated article discussing the resonance
energy of six-member nitrogen heterocycles. Dis-
cusses pyridine, pyrazine, heterocycles with con-
densed rings. Quantum mechanical methods were used
on six-member nitrogen heterocycles. These experi-
ments were conducted at the Physical Chemical Insti-
tute imeni L. Ya. Karpov in Moscow. Prof Ya. K.
Syrkin aided greatly with the experiments.

2419

DYAKTINA, M. YE.

PA 60T11

USSR/Chemistry - Heterocyclic Compounds Dec 1947
Chemistry - Isomerism

"Tautomerism of Derivatives of Heterocycles,"
M. Ye. Dyaktina, 4 pp

"Dok Akad Nauk SSSR, Nova Ser" Vol LVIII, No 7

Loss of energy of resonance in tautomerization of derivatives of heterocycles is greater than change of energy of resonance in tautomerization of derivatives of hydrocarbons. Therefore, noticeable inclination toward tautomerization will be observed only in oxide derivatives because of the great gain in energy of bond. Submitted by Academician A. N. Frankin, 16 Jun 1947.

60T11

1st and 2nd groups		PRE-TEST AND PROPERTIES INDEX		1st and 2nd groups																																																													
<p><i>CA</i></p> <p>Free radicals with hetero atoms. <i>Ad. Lyndine, Khim. (Mikhail Khim. (J. Gen. Chem.) 10, 511(1948).—</i> The magnitude of the energy change on disocn. of dimers into free radicals for a system with hetero atoms differs from the corresponding value for hydrocarbons because of the difference in bond energies of C—C and X—X and the variation of resonance energy on conversion of a hydrocarbon radical into a radical with heteroatoms. For radicals with the hetero atom bearing an unpaired electron, the magnitude of the energy gain on disocn. increases with increase in δ (ratio of the coulomb energy of the heteroatom X to that of the carbon atom C) and in γ (ratio of the value of the exchange integral for C—X to that for C—C) and noticeably exceeds the corresponding value for pure hydrocarbon radicals. The increase in addnl. energy of radicals assoc. with increase in stability of the C—X bond is explained by the increase in energy and by the increased contribution of structures in which an unpaired electron resonates between different atoms of the system. With values of the parameters, δ and γ, corresponding to a N atom, the gain in resonance energy may cause disocn. of dimers in the presence of 4 aryl groups. In the case of O two substituting groups suffice. This explains the disocn. of tetraarylhydrazines and aromatic peroxides.</p>																																																																	
<p>In systems with two hetero atoms γ increases the energy gain and δ decreases it. In radicals in which the hetero atom is in the added group and sepl. from the atom bearing the unpaired electron by an odd number of atoms, introduction of γ causes a reduction in the energy gain on disocn. but δ does not alter these values so that with α- and γ-pyridylmethanes the tendency toward disocn. must be less than with arylethanes. If the hetero atom is located adjacent to the atom bearing the unpaired electron, γ increases the gain in energy but δ somewhat decreases it. In radicals in which the hetero atom is sepl. from the atom bearing the unpaired electron by an even number of atoms, the gain in energy in disocn. is similar to that of the corresponding hydrocarbon radicals.</p>																																																																	
<p>R. W. Buncker</p>																																																																	
<p>ASB SLA METALLURGICAL LITERATURE CLASSIFICATION</p>																																																																	
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DYATKINA, M. Ye.

PA 65T20

USSR/Chemistry - Resonance, Energy of Mar 1948
Chemistry - Valency

"Quantitative Conformity of Methods of Molecular
Orbits and Valence Structures," M. Ye. Dyatkina,
Physicochem Inst imeni Karpov, Moscow, 13 pp

"Zhur Fiz Khim" Vol XXII, No 3, pp 286-287

Compares the energies of resonance calculated
according to the methods of molecular orbits and
valence structures. Submitted 10 Jun 1947.

65T20

DYATKINA, M.

PA 68T20

USSR/Chemistry - Heterocyclic Compounds May 1948
Chemistry - Double Bonds

"Energy of Stimulation of Systems With Conjugate Double Bonds and Heterocyclic Atoms," M. Dyatkina, Phys Chem Inst imeni L. Ya. Karpov, Moscow, 12 pp

"Zhur Fiz Khim" Vol XXII, No 5, pp. 549-560

Energy of stimulation of a series of systems with heterocyclic atoms was calculated by means of modified molecular orbit method, i.e., calculating increased energy of electron at heterocyclic atom (parameter δ) and increased resonance integral of link Cx (parameter γ). Results are shown in tabular form and analyzed. Submitted 9 Jul 1947.

68T20

S. Samvilov and M. Diatkina, Concerning the configuration of polyphenyls and triphenylmethyl. Pp. 1294-1301.

By the method of molecular orbitals are calculated the resonance energy of diphenyl, triphenyl and triphenylmethyl and various angles of rotation of the rings relative to the planar configuration. A relation has been found between the inter-action energy of the ortho-atoms of hydrogen in the above molecules and the angle of rotation. In the most stable configurations of molecules, the angle between phenyl rings must be about 30° .

The Karpov Physical Chemical Inst.
Moscow
April 9, 1948

SO: Journal of Physical Chemistry (USSR) 22, No. 11, 1948

The basicity of heterocycles. Al. E. Dyatkina. *Doklady Akad. Nauk S.S.S.R.* 59, 517-518 (1948) (in Russian).
 Differences in the basicity of heterocycles, particularly its decrease with increasing no. of condensed benzene ring (pyridine, quinoline, acridine) and its dependence on the position of the hetero atom (quinoline, isquinoline), are interpreted in terms of change of resonance on transition to the ionic state. In particular, on transition of the N atom to N^+ , the excess of the strength of the σ -bond CN over the CC bond is further increased, and, inasmuch as in heterocycles with the hetero atom in a system of conjugate bonds, as in pyridine, the resonance energy increases with increasing resonance integral γ , whereas it decreases in the case of quinone imine, ionization is accompanied by a gain of energy in the former case, and pyridine is more strongly basic ($K_b = 1.71 \times 10^{-5}$) than quinoline

($K_b = 1.7 \times 10^{-6}$). In general, the basicity is the higher the stronger the increase of the resonance energy with increasing γ . The decrease of basicity in the order pyridine, quinoline, acridine, is in qual. agreement with this postulate, the increase of resonance energy with γ increasing from ∞ to 2, being 4-0.49, 0.37, and 0.30, resp., between quinoline and acridine, the corresponding values are 0.40 and 0.13, resp.; hence, the latter should be appreciably lower, which is borne out by the calculated values from electrostatic data, whereas there is some discrepancy with the potentiometric value for quinoline. The same postulate permits prediction of at least the order of decreasing basicity for heterocycles for which no data are available. H. Thoen

Hybrid orbitals for the coordination numbers 7 and 9. M. G. Shermazan and M. B. Dyatkina. *Doklady Akad. Nauk S.S.S.R.* **77**, 75-8 (1961).—Of the two known configurations with a coordination no. 7, the configuration of ZrF_7^{3-} , an octahedron with one extra atom in the center of a face, symmetry C_{3v} , can arise through the hybridization d^2sp^3 and d^3sp^2 ; the type TaF_7^{3-} , a triangular prism with one extra atom in the center of a square face, symmetry C_{2v} , can arise through the hybridizations d^2sp^3 , d^3sp^2 , and d^4sp . Two new configurations are calculated by the method of

Kimball (C.A. 34, 1524¹), by group-theoretical calcn. of the irreducible representations based on the at. orbits s, p, d, f , and then on the valence σ -orbitals. A configuration with the coordination no. 7, with the σ -bonds directed towards the corners of a pentagonal bipyramid, symmetry D_{5h} , can arise through the hybridizations sp^2d , sp^2f , sp^2df , sp^2d^2 , sp^2df^2 , sp^2d^2f , sd^2f^2 ; of these only one does not involve f electrons. A configuration with the coordination no. 9, a trigonal prism with 3 extra atoms over the centers of the rectangular faces, symmetry D_{6h} , can arise through the hybridizations sp^2d , sp^2d^2 , sp^2d^3 , sp^2d^4 , sp^2d^5 , sp^2d^6 , sp^2d^7 , sp^2d^8 , sp^2d^9 , sp^2d^{10} , sp^2d^{11} , sp^2d^{12} , sp^2d^{13} , sp^2d^{14} , sp^2d^{15} , sp^2d^{16} , sp^2d^{17} , sp^2d^{18} . N. Thon

CP

2

Resolutions of the colloquium on the theory on chemical structure in organic chemistry held in Moscow (June, 1951). *Zhur. Fiz. Khim.* 25, 988-91 (1951).—Ya. K. Syrkin, M. E. Dyatkina, M. V. Vol'kenshteln, A. I. Kiprianov, and others are criticized for their idealistic and mechanistic concepts of resonance. The Conference calls upon the chemists and scientists working in related fields of physics, to develop creatively the theory of chem. structure of A. M. Butlerov along the principles of dialectic materialism under the guidance of the work of I. V. Stalin.

M. B.

1. SYRKIN, YA. K., DYATKINA, M. YE.
2. USSR (600)
4. Mesomerism
7. On the "resonance theory or mesomerism." Izv AN SSSR Otd khim nauk. No 6 1952.
9. Monthly List of Russian Accessions, Library of Congress, April 1953, Uncl.

DYATKINA M. YE.

238T7

USSR/Chemistry - Valency

Feb 52

"Valence Direction of Valency Bonds for Coordination Numbers Six and Eight," M. G. Shirmazan and M. Ye. Dyatkina, Physicochemi Inst imeni L. Ya. Karpov

"DAN SSSR" Vol 82, No 5, pp 755, 756

Arrangement of bonds having symmetry of C_{3v} cannot occur without the participation of f-electrons. Since the Ta atom lacks f-electrons, it is not likely that it has the TaF_8^3 structure indicated in the literature. Presented by Acad A. N. Frumkin 13 Dec 51

238T7

DIAGRAM, p. 15.

USSR/Chemistry - Valency

Apr 53

"Directed Valency With Participation of f-Electrons," M. G. Shirmazan, M. Ye. Dyatkina, Phys-Chem Inst im L. Ya. Karpov, Moscow

Zhur Fiz Khim, Vol 27, No 4, pp 491-494

Found the directions in which there is maximum concn of the electron cloud. Detd max values of f-functions and carried out series expansions of f-functions to obtain irreducible representations of different symmetry groups. Found the directed valencies in which s,p,d, and f electrons participate for 22 different dispositions of σ - bonds at coordination numbers 2-9.

270718

DYATKINA, M. E.

USSR/Chemistry

Authors : Dyatkina, M. E.

Title : Thermodynamic functions of normal alcohols (propyl, butyl and ethylene glycol).

Periodical : Zhur. Fiz. Khim. 28, Ed. 3, 377-388, March 1954

Abstract : The thermodynamic functions of normal alcohols (propyl, butyl and ethylene glycol) were calculated. The following molecular parameters were adopted in the calculation: molecular spaces C-C 1.54 Å, C-H 1.09 Å, C-O 1.42 Å, O-H 0.96 Å, the angles at atoms C are tetrahedral, angles at C-O-H 105°. At these parameters in the case of propyl alcohol the main axis x forms an angle of 27°56' with the axis parallel to the lines of bonds H₃C-CH₂ and CH₂-O; the axis y is perpendicular to the plane CCCO. The values of the atom coordinates relative to the main axes are given in table. Seven references; 1 USSR. Tables.

Institution :

Submitted : November 27, 1952